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THE ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

EDITED BY

GEORGE E. HALE
Mount Wilson Observatory of the Carnegie Institution of Washington

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Yerkes Observatory of the University of Chicago

HENRY G. GALE
Ryerson Physical Laboratory of the University of Chicago

DECEMBER 1920

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THE
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VOLUME LII DECEMBER 1920 NUMBER 5

REVISION OF THE SERIES IN THE SPECTRUM OF CALCIUM

By F. A. SAUNDERS

ABSTRACT

Series in the spectrum of calcium.—A study of the triplet and singlet systems, based on recent observations including some *fifty new lines*, has led to the extension of most of the series, the calculation of the limits with greater precision and the identification of various combination series. The diffuse series of triplets is extended to 15 terms and is shown to exhibit curious anomalies. Altogether, four triple-series of each system and eight probable combination series are given and also indications of three possible inter-system combination series.

In the course of a study of the series in the spectrum of Ca some new data have been obtained which it now seems worth while to summarize in a brief article. A knowledge of the structure of this spectrum is much to be desired. While it is relatively simple, it is less so than He or Na, and those features which are new may guide us toward the solution of still more complex spectra. It has not yet been possible to classify all the lines in the Ca spectrum, but a considerable advance in this direction has been made. More observations are needed, especially in the infra-red, where the experimental difficulties are formidable.

The sources used in this work have been the vacuum lamp,[1] the vacuum arc, the hot quartz vacuum tube, or oven, besides all

[1] *Astrophysical Journal*, 40, 377, 1914.

the more usual ones. Observations have been kindly furnished by Dr. A. S. King, from plates taken with his vacuum oven; and Professor H. M. Randall has contributed valuable (as yet unpublished) observations in the infra-red region. Certain facts in regard to the Zeeman effect for Ca the writer owes to Professor Paschen and his collaborators. The most valuable among the recent published sources of information about the Ca spectrum has been the work of Crew and McCauley,[1] which covers the vacuum arc spectrum very thoroughly within a certain range, and with admirable precision. Their wave-lengths, on the international system, have been taken as a basis for all the lists here given, though mention should also be made of the work of Holtz,[2] done, unfortunately, on the arc in air, where the diffuseness of some of the lines prevents accurate measurements. Lorenser's dissertation[3] furnishes observations in the red, and a partially successful attempt at a classification of some of the lines into series.

The spectrum of Ca consists of three systems of series, each containing at least four types of series, together with combination series derived from these. Attention is here limited to two of these systems, the triplets and the single lines or singlets. Inter-system series, obtained by combinations between these two, are known, but no such combinations involving the third system, that of pairs, have been found. This is one of many facts that lead to the belief that the pair system is given by a different vibrating mechanism, presumably ionized Ca, or Ca^+.

The four type-series in each system are called the principal, sharp, diffuse, and fundamental series. The notation used has already been explained.[4] The symbol (mp), for instance, stands for one of the "terms" (wave-number differences between limit and individual line)[5] of the principal series of triplets, m having and integral value from unity up; the corresponding symbol (mP) refers to the principal series of singlets. The numeration adopted

[1] *Astrophysical Journal*, **39**, 29, 1914.

[2] *Zeitschrift für wissenschaftliche Photographie*, **12**, 101, 1913.

[3] Tübingen, 1913; review, *Astrophysical Journal*, **41**, 323, 1915.

[4] *Astrophysical Journal*, **41**, 323, 1915.

[5] In the language of the Bohr theory, each term is proportional to the energy of the radiating electron in one "stationary state."

for m varies somewhat among different writers. Paschen uses 1.5, 2.5, etc., for the values of m in the terms (mS), while Fowler and others prefer whole numbers. Theory furnishes as yet no safe guide in this matter. The lowest value of m in (mp) is taken as 2 by Paschen, and as 1 by Fowler, and in what follows. For the diffuse series Paschen begins with 3, Fowler with 2, while I have preferred 1 for the convenience of having m always the same as the number of the corresponding series member, counting from the beginning of the series.

The results are presented under the headings of the individual series, classified under the triplet system, the singlet system, and inter-system combinations.

THE TRIPLET SYSTEM

Principal series of triplets: $(1s)-(mp)$. The first member of this series is also the first member of the sharp series; its lines are λλ 6162.18; 6122.22; 6102.72. The corresponding terms are 33988.7; 34094.6; 34146.9. The next triplet in this series has not yet been satisfactorily observed, but its position can be fixed through the combination $(1d)-(2p)$ given below. The predicted wave-lengths are 19852.7, 19932.2, 19959.7; two lines have been observed at 19856.3 and 19935.2; the third line is the faintest of the three and has not yet been found. This triplet is entangled with the first member of the diffuse triplets, and has not yet been satisfactorily resolved. The third triplet of the series has not been observed; it must be very faint, as a two-hour exposure of the vapor-lamp spectrum with a large prism spectrograph, using a dicyanin-stained plate, gave no trace of it. Its position can be calculated, however, from the combination $(1d)-(3p)$ given below, and the calculated wave-lengths are 9108.71, 9105.40, 9098.93; of these the last is the strongest. The fourth member of this series cannot be calculated with certainty, as the combination $(1d)-(4p)$ has not been identified satisfactorily; but there are indications pointing to a value 4342.7 for the term $(4p)$, the three values of which would be very close. If this is correct the triplet would be near λ 7448.2, but it has not been found.

This series was first given by Paschen, though incompletely. It is a faint series, in spite of its name, and its lines should, by analogy, be very diffuse in sources in air; it retains the name "principal" merely on account of its relationship with the sharp series, which is that characteristic of principal series in the spectra of other elements, such as Na. It is to be noted that Popow[1] selected a value for $(2p)$, or in his notation $(3p)$, which is different from the one here given. His choice cannot hold, for reasons which I have recently pointed out[2] in the analogous case of Ba. The term to which he calls attention must belong to a still unknown series.

Sharp series of triplets: $(1p)$–(ms).—The accompanying tables give the wave-lengths of the lines of this series in international units, together with the wave-number differences within each triplet, which should remain constant, and the "terms." In con-

TABLE I

SHARP SERIES OF TRIPLETS $(1p)-(ms)$. LIMITS 33988.7; 34094.6; 34146.9

λ I.A.	$\Delta\nu_1$	λ I.A.	$\Delta\nu_2$	λ I.A.	Terms	m
6162.18	105.9	6122.22	52.2	6102.72	17765.1	1
3973.72	105.9	3957.05	52.2	3948.90	8830.3	2
3487.61	106.0	3474.77	52.1	3468.48	5323.8	3
3286.06	105.8	3274.66	52.1	3269.09	3565.6	4
3180.52	105.8	3169.85	52.1	3164.62	2556.2	5
3117.66	105.9	3107.39	52.2	3102.36	1922.4	6
3076.99	105.7	3067.01	52.7	3062.05	1498.6	7
3049.01	105.8	3039.21	50.8	3034.52	1200.3	8
3028.97	104.9	3019.37			982.5	9
3014.01					819.8	10

nection with this table it should be noted that the line λ 3076.99 was measured by Crew and McCauley, and that the lines λλ 3049.01 3039.21, 3028.97, 3019.37, and 3014.01 are new. The line 3034.52 is most probably a diffuse series line, which nearly coincides with the fainter sharp series line to be expected in this neighborhood.

This series was one of those first found in Ca. It is of medium strength, but its outer members fade rapidly and become diffuse

[1] *Annalen der Physik*, **45**, 160, 1914.

[2] *Astrophysical Journal*, **51**, 23, 1920.

in air sources. A long column of luminous vapor at a low pressure is required to give the new lines.

Diffuse series of triplets: $(1p)-(md)$.—This is the most obvious series in the Ca spectrum. Its lines are given in Table III. It should be noted that the lines λλ 3109, 3108, 3099, 3080, 3071.58, 3055.32, 3045, 3034, 3024, and 3018 were measured by Crew and McCauley but are here classified for the first time. The lines

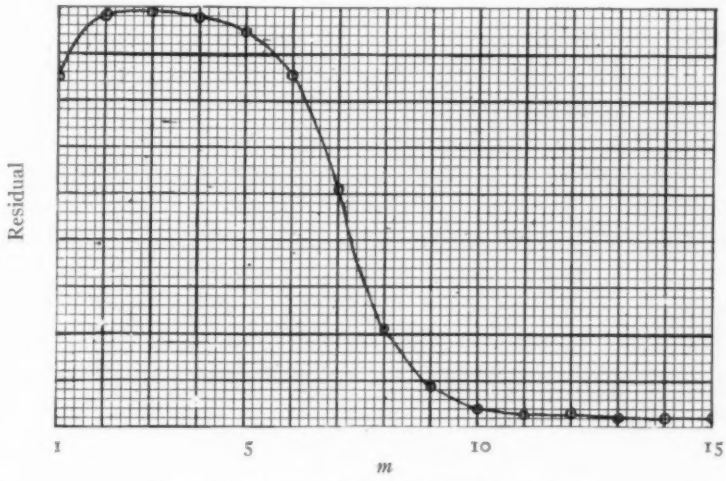

FIG. 1.—Curve of Residuals for Ca $(1p)$–(md)

λλ 3095, 3081, 3071.97, 3067, 3055.55, 3020, 3006, 2996, 2988, and 2982 are new.

This series exhibits a remarkable type of irregularity, similar to that already found in the narrow triplets of Ba, and quite unsuspected from previous observations. The usual diffuse triplet really consists of six lines, the first three being quite close, and forming the first and strongest "line" of the triplet; the middle line on closer inspection proves to be a close pair. The narrow triplet formed by the first three behaves like a principal series in itself. Not only does it shrink to a single line in passing out toward the limit of the series, but its intensities are arranged in the manner

TABLE II

DIFFUSE SERIES OF TRIPLETS $(1p)-(md)$. LIMITS SAME AS IN SHARP SERIES

λ I.A.	$\Delta\nu_1$	λ I.A.	$\Delta\nu_2$	λ I.A.	Terms	m
19917.3	105.6	19506.8	52.1	19310.3	28969.1	1
19864.3	106.6	19452.6			28955.2	
19777.1					28933.5	
4456.61	105.9	4435.67	52.1	4425.43	11556.4	2
4455.88	105.9	4434.95			11552.6	
4454.77					11547.0	
3644.99	106.0	3630.97	52.0	3624.11	6561.4	3
3644.76	105.9	3630.75			6559.7	
3644.40					6556.9	
3362.28	105.8	3350.36	52.2	3344.51	4255.5	4
3362.13	105.9	3350.20			4254.0	
3361.92					4252.2	
		3215.33	52.3	3209.93	3002.4	5
3226.13	105.8	3215.15			3000.6	
3225.88					2998.2	
		3141.16	52.4	3136.00	2268.2	6
3151.28	106.0	3140.78			2264.5	
3150.75					2259.3	
		3100.22	51.4	3095.29	1848.9	7
3109.51	105.4	3099.34			1838.7	
3108.58					1828.8	
		3071.97	52.6	3067.01	1551.2	8
3081.55	105.4	3071.58			1547.0	
3080.82					1539.1	
				3041.05	1272.7	9
3055.55	105.1	3045.75			1270.7	
3055.32					1268.2	
3034.52	104.4	3024.93	52.3	3020.15	1045.4	10
3018.55					869.6	11
3006.22	105.9	2996.67			733.8	12
2996.67					627.9	13
2988.98					541.0	14
2982.89					473.5	15

of principal series. It is also connected with another series, the fundamental, in precisely the same way that the principal is connected with the sharp (the Rydberg-Schuster law). The shrinking of these little triplets is in most cases progressive and regular. I have recently made a special examination of the corresponding triplets of Zn and of Cd and found no irregularity, even though the vacuum source which was used revealed a large number of new series members. But in the case of this series in Ca, the shrinking is checked at the fourth member, and the group then widens progressively in the three following members, subsequently shrinking rapidly. All this happens without disturbing the constancy of the differences of wave-number, as is shown in the tables. The "curve of residuals" also is far from simple, as shown in Figure 1, though it is smooth, indicating that the observed perturbations are real; this means that no simple formula can be made to fit the series. Another anomaly is furnished by the intensities; the eighth triplet is unduly faint, or the few following unduly strong.

Fundamental series of triplets: $(1d)-(mf)$.—This series has been considerably extended, and its limit is here given with much greater precision than before. Its terms are really complex, prob-

TABLE III

FUNDAMENTAL SERIES OF TRIPLETS $(1d)-(mf)$. LIMITS 28933.5; 28955.1; 28968.8

λ I.A.	$\Delta\nu_2$	λ I.A.	$\Delta\nu_1$	λ I.A.	Terms	m
4585.92 4585.87	21.5	4581.41	13.6	4578.57	7133.9	1
4098.55	21.5	4094.94	13.7	4092.65	4541.5	2
3875.81	21.8	3872.55	13.5	3870.51	3139.5	3
3753.37	21.5	3750.35	14.1	3748.37	2298.1	4
3678.24	21.6	3675.31	13.8	3673.45	1754.1	5
3628.60	22.1	3625.69	12.0	3624.11	1382.3	6
3594.08	21.8	3591.26	13.8	3589.49	1117.7	7
3568.91	24.3	3566.12	13.9	3564.35	923	8
3550.03	23.5	3547.38	14.3	3545.58	774	9
3535.55					660	10

ably triple, but the lines are too close for measurement in all but one case, resolved by Janicki. From λ 3628 on, all the lines in the table of this series are new.

COMBINATION SERIES IN THE TRIPLET SYSTEM

Series $(1d)-(mp)$.—If we subtract the three terms $(2p)$, which are 12729.4, 12749.5, and 12756.4, from the three terms $(1d)$ given above, we obtain nine numbers, of which six give real lines in a narrow group in the orange, first completely observed by Lorenser. This is the second member of this series, the first being the first of the diffuse triplets, taken with negative sign. Since the principal series lines converge to a single limit, the present series, which begins as a complex group, should converge to a narrow triplet. The third member of the series is faint, but comes out well in the vapor lamp spectrum, and in the vacuum arc. Its lines, with one exception, are in the list of Crew and McCauley. They are λλ 4512.28, 4507.85, 4509.45, 4505.00, 4506.62, 4507.42, arranged in the order of their group positions. The fourth member must be extremely faint. Lines at λλ 4065.44 and 4062.49 seem to belong to it, but it was impossible to complete the group.

Series $(2d)-(mf)$.—This series lies in the ultra-red and was given by Paschen. Only one member has been observed, a close triplet at λλ 22655.9, 22624.6, and 22610.0 $(m=2)$. Randall (unpublished) has found tentative indications of a second member near λ 14278.

Series $(2p)-(md)$.—This is a possible but still doubtful series in the ultra-red. It probably takes the form of groups of six lines. Three, at λλ 16200.0, 16162.2, and 16144.8, have been observed, which seem to form part of such a group, but it is not fully resolved. The next member has not been found.

THE SINGLET SYSTEM

Principal series of singlets: $(1S)-(mP)$.—This series is the one formerly called *SL1* and it has been known for some time.[1] It contains the flame line λ 4227, and most of its lines are of the same character, that is, easily reversed. There is an anomaly in the intensities, however; the second line is much too faint, and does not reverse. A similar peculiarity appears in the corresponding series in Sr and in Ba. The weak line must belong to this series, as its "term" leads to combinations which exist. The "curve of

[1] *Physical Review*, **1**, 332, 1913.

residuals" for this series has a point of inflexion, as Lorenser pointed out. The terms given in the table for this series are averages obtained from this series and the series $(1D)$–(mP) given below.

Sharp series of singlets: $(1P)-(mS)$.—This series must, by analogy, be a fairly strong one, but it is difficult to settle its course with certainty. The information furnished by the Zeeman effect fails to separate this from any other series of singlets, and observations are lacking in the infra-red, where particularly needed. There are no constant differences to guide our choice of lines. Lorenser

TABLE IV

SYSTEM OF SINGLET SERIES

m	PRINCIPAL $(1S)-(mP)$		SHARP $(1P)-(mS)$		DIFFUSE $(1P)-(mD)$		FUNDAMENTAL $(1D)-(mF)$	
	λ I.A.	Terms	λ I.A.	Terms	λ I.A.	Terms	λ I.A.	Terms
1.....	4226.73	25652.4	4226.73	49304.8	(5.55μ)	27455.3	4878.13	6961.3
2.....	2721.65	12573.1	10345.0	15988.2	7326.10	12006.3	4355.10	4500.0
3.....	2398.58	7625.9	5512.98	7518.4	5188.85	6385.5	4108.55	3122.6
4.....	2275.49	5371.4	4847.29	5028.0	4685.26	4314.7	3972.58	2289.7
5.....	2200.78	3879.6	4496.16	3417.3	4412.30	2994.7	3889.14	1749.8
6.....	2150.78	2824.6	4312.31	2469.4			3833.96	1379.8
7.....	2118.68	2120.3	4203.22	1867.7			3795.62	1116.3
8.....	2097.49	1638.2	4132.64	1461.5			3767.42	919.3
9.....	2082.73	1305.9	4084.5	1176.0				
10.....	2073.04	1071.6						
11.....	2064.77	888.5						

sketched out an arrangement for the beginning of this series in the expectation that later observations would yield lines to complete the series as outlined. Such lines do not, however, appear, and instead we have others which fail to fit into his scheme.

The first term of the series must be the limit of the principal series; the limit of the series is likewise known. Hence the second term may be calculated, roughly, by one of the series formulae. Any one of two or three lines in the infra-red might serve as the corresponding line, the second of the series; the one here chosen works out best, and the rest of the series follows with reasonable certainty. Two of the lines run parallel to two ultra-violet lines, which must belong to the combination series $(1S)-(mS)$ given

below. This greatly strengthens the foundation on which the arrangement rests. The curve of residuals is not a simple one, but is simpler than that given by any other grouping of the available lines. The Zeeman effect for these lines, as far as known, is correct, namely, normal triplets. The last half of the lines in the table are new, having been obtained from vacuum sources. The last one is very doubtful.

Diffuse series of singlets: $(1P)-(mD)$.—The limit of this series is, of course, known, being the term $(1P)$ of the principal series. In spite of this fact its course would be difficult to discover were it not for the existence of a parallel series in the ultra-violet, having the same terms. The last three lines are thus classified as belonging together, though the series to which they belong is not identified in this way. The line here given at the head of the series has not yet been observed, and involves a negative frequency. Analogy with Ba points to its existence, and the negative frequency offers no special difficulty, if one is willing to admit the possibility of such a thing in other series. For instance, the first member of the principal series of most elements is also a member, but with negative frequency, of the sharp series. Something similar occurs with the diffuse triplets of Ba, and the diffuse pairs of Ca, Sr, and Ba. It is evidently common with diffuse series.

The limit of the two series formerly known as $SL2$ and $SL3$ is $1/\lambda = 27455$. This number must, according to the combination principle of Ritz, itself be a term belonging to some series in the Ca spectrum. There is no series but this one to which this term can belong without producing a quite unreasonable sequence of terms. This must be the term $(1D)$, the first term of the diffuse series, and the limit of the fundamental. An analogous conclusion may be drawn for Sr, and has already been given for Ba. The identification of this series as the diffuse is further strengthened by the fact that Takamine[1] has observed that λ 4685, one of the lines of this series, is affected by an electric field; and it seems to be true that the Stark effect is greater for diffuse series than for any others. The identification of the series $SL3$ as the fundamental follows from the choice of the term $(1D)$ above, and appears also to be reasonable,

[1] *Kyoto University Memoirs*, **3**, 173, 1918.

since its terms, in common with those of other fundamental series, have values not far from those of the hydrogen series.

Lorenser has outlined the beginning of this series, but, as in the case of the preceding, incorrectly. He began it with a negative-frequency line, as I have done, but a different one, and one which leads to no combinations, and has apparently no justification. He also included a line λ 6462, which certainly has the wrong Zeeman effect. Two of his lines, λλ 5189 and 4685, are, however, included in my list.

Fundamental series of singlets: $(1D)-(mF)$.—The foregoing argument leads to the identification of this series, formerly known as SL_3. Its lines are here given with greater precision, and the last three are new. The limit is much more accurately determined than before. The similarity of the terms of this series and those of the fundamental series of triplets makes it possible to obtain a useful check on the values of the limits of both series, furnishing a direct connection between the triplet and singlet system, in addition to that given by inter-system combinations. The limits of all the series given in this paper have been adjusted to the best values consistent with these relations.

COMBINATION SERIES IN THE SINGLET SYSTEM

Series $(1D)-(mP)$.—This is the series formerly called SL_2. Its wave-lengths are as follows: λλ 6717.69, 5041.61, 4526.94, 4240.46, 4058.91, 3946.05, and 3871.54, of which several are now more accurately known, and the last is new. The series is of medium strength in vacuum sources, but faint and diffuse in air. The first line of this series is probably at 5.55μ, and is the first line of the diffuse series also. It has not yet been observed.

Series $(1S)-(mD)$.—The wave-lengths of this series run: λλ 4575.43, 2680.36, 2329.33, and 2221.91, as far as they have been observed. It is a faint series. The second line coincides almost exactly with a line of the principal series of Na, which is nearly always present as an impurity. I have inferred the presence of the Ca line only from the fact that the line was slightly stronger than one would expect; the identification is therefore somewhat

doubtful. The last two lines were found only on plates taken with the arc in air, and their diffuseness prevents accurate measurement. A photograph reproduced in this *Journal*[1] shows some of them.

Series $(1S)-(mS)$.—This series is similar in character to the preceding. Its first line $(m=2)$ should appear very near to the strong line λ 3000.87, but could not be observed, probably on account of the spreading of its strong neighbor. The next three lines are at λλ 2392.22, 2257.40, and 2177.8.

Series $(1P)-(mP)$.—This combination is common in other spectra. Here it is very faint, and somewhat doubtful. The first line appears to be λ 7645.25, observed by Lorenser. The second line should appear near λ 5546, in a region usually "occupied" by a band. The third line was found in its predicted position at λ 4929.25, in vacuum sources.

Series $(2S)-(mP)$.—For $m=2$, the calculated value of ν is 3415; Randall has observed a line at 3412. For $m=3$, the calculated value of ν is 8362, the observed 8359. For $m=4$ no line has been found. The series is still doubtful.

Series $(1D)-(mS)$.—For $m=3$, the calculated value of ν is 19936.9, and there is a line at 19935.2, observed as a faint and very diffuse line in the arc in air. The next line is not found.

INTER-SYSTEM COMBINATION SERIES

Series $(1S)-(mp_2)$.—The first line of this series appears in the vacuum oven as quite a strong line; it occurs at λ 6572.78, and was identified by Paschen. The next line is very faint, but was observed at λ 2734.82, calculated λ 2734.84. The third line could not be found.

Series $(1p_2)-(mS)$.—This series may exist. Its first line has not yet been found, but the second occurs as a faint line at precisely the predicted place, λ 3761.72. The combination $(1p_1)-(3S)$ also occurs, but this is probably merely a numerical coincidence.

Series $(1D)-(mp)$.—This series is very doubtful, but is included because the combinations $(1D)-(2p_1)$, $(1D)-(2p_3)$, and $(1D)-(3p_3)$ lead approximately to faint and diffuse lines in the arc in air. The coincidences may be accidental.

[1] *Astrophysical Journal*, **43**, 238, 1916.

SUMMARY

The spectrum of Ca consists of three systems of series. Each system contains four type-series, and combinations formed from these. The triplet and singlet systems are here studied, on the basis of new observations, mainly from vacuum sources. In the triplet system, the type-series are given, several new lines being added, and the limits calculated with considerable precision. The diffuse series of triplets is shown to exhibit certain curious anomalies. Three combination series in this system are probable. In the singlet system also the four type-series are given, and five combination series suggested. There are also indications of three series formed by combinations between the triplet and singlet systems.

JEFFERSON PHYSICAL LABORATORY
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THE EXCITATION OF LIGHT BY CATHODE RAYS IN AIR

By GORDON S. FULCHER

ABSTRACT

Light excited by cathode rays in air.—A beam of cathode rays, after passing through a hole in the anode of the discharge tube in which the rays were produced, was placed at the focus of the collimating lens of a spectrograph and the *intensity of the nitrogen bands* excited was determined for various discharge potentials and for various distances apart of the electrodes. The results show that, unlike canal rays, cathode rays in passing through nitrogen excite less light per collision the greater their energy, at least *for the range of speeds corresponding to from 1500 to 3500 volts.* Since the rays used were not homogeneous, the exact law of variation cannot be determined from the data obtained, but the results indicate that the light per collision varies inversely as a power of the speed somewhat less than the second; and it is pointed out that if, as is quite possible, the light intensity per collision varies with the speed in the same way as the chance of ionization per collision, then the light intensity per ionizing collision is independent of the speed.

Since it is probable that much of the light we observe in connection with the discharge of electricity through gases is directly due to the bombardment of gas molecules by cathode and canal rays, it is of interest to determine how the quality and intensity of the light emitted by a given gas depend on the nature and speed of the bombarding rays. Some years ago, experiments with canal rays in air[1] showed that the intensity of the light emitted by nitrogen molecules per collision is directly proportional to the mean energy of the bombarding canal rays, at least for the range of speeds corresponding to cathode falls between 1000 and 5000 volts. To determine whether a similar law holds in the case of bombardment by cathode rays, the following experiments were carried out at the University of Wisconsin during 1916.[2]

METHOD AND APPARATUS

The method adopted was similar to that used for canal rays. A diagram of the apparatus is shown in Figure 1. Cathode rays produced by a discharge were shot through a hole in the anode into

[1] *Astrophysical Journal*, **33**, 28, 1911.

[2] The results were presented at the Chicago meeting of the American Physical Society, December 2, 1916.

a space where the light they excited could be observed, and thence into a Faraday cylinder connected through a galvanometer to the anode.

The immediate purpose of the experiment was to determine how the intensity of the light emitted per cathode ray per unit of gas pressure varied with the discharge potential and also with the distance apart of the electrodes. There were, then, five quantities to measure. The number of rays involved in exciting the light was determined by reading the galvanometer in series with the Faraday cylinder. The gas pressure was measured with a McLeod gauge connected directly to the observation chamber. The discharge potential was obtained by means of a calibrated Kelvin electrostatic voltmeter, and a scale gave the electrode separation, which could be adjusted to any desired value by softening the wax which held the wire supporting the cathode.

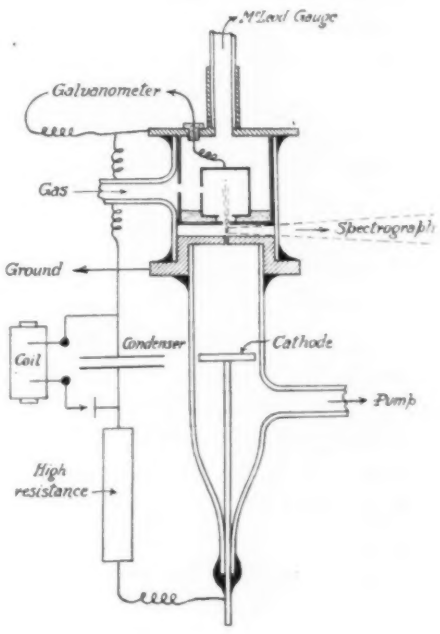

FIG. 1.—Apparatus

To measure the intensity of the nitrogen bands excited, a Hilger spectrograph with slit removed was placed so that the cathode beam in the observation chamber was at the focus of the collimating lens, and thus spectrograms were obtained with lines each about 2 mm wide, broad enough so that the density of the image could be measured with fair accuracy by means of a spectrophotometer. As was to be expected from previous qualitative results,[1] the spectrograms showed only the negative nitrogen bands λ 3914 and λ 4278; and since their relative intensity was constant, the

[1] *Astrophysical Journal*, **34**, 388, 1911.

density of the stronger, λ 3914, was used in calculating the light intensity. To insure uniform treatment during development, a series of exposures was made on the same plate; and to minimize the correction for the well-known lack of proportionality between image-density and illumination, the times of exposure were adjusted after preliminary trials so as to make the corresponding images on each plate come out with about the same density. Then the desired light intensity was taken to be proportional to the density, corrected slightly according to the characteristic curve of the Stanley plate used, divided by the time of exposure. A special test indicated that the error introduced by the assumption that for a given image-density the light intensity was inversely proportional to the time of exposure is small.

Taking the number of collisions with nitrogen molecules per centimeter as proportional to the number of rays multiplied by the gas pressure, the light emitted per collision is evidently proportional to the image-density divided by the product of the time of exposure, the galvanometer current, and the pressure, that is, to D/pIt.

To secure a continuous discharge, the same arrangement of induction coil, rectifying spark-gap, capacity, and high resistance was used as in previous work. Also, as before, conditions were kept constant during an exposure by maintaining a constant stream of dry gas through the apparatus by the use of a gas reservoir, capillary tube, and Gaede mercury pump. Mercury and other vapors were removed from the gas by means of a liquid-air trap.

EXPERIMENTAL RESULTS

The following table contains two series of measurements made when the electrodes were respectively 30 mm and 40 mm apart, and also two series in which the position of the cathode was varied between exposures so as to make the separation of the electrodes in one series 5/3 and in the other 7/6 of the length of the cathode dark space for the particular pressure used in each case. The letters *a*, *b*, etc., indicate the order in which the exposures were made; 32, 34, etc., are the plate numbers.

An examination of the figures in the last two columns of the table shows that in every case except 32*b*, the light excited per collision, instead of increasing with the discharge potential as for canal rays, decreases, whether the separation of the electrodes

TABLE I

Number	d	I	D'	D	t	p	V	D/pIt
32 *b*....	30	4.0	.60	.62	16	.139	910	.070
d....	30	8.1	.72	.72	11.5	.107	1155	.072
a....	30	6.9	.74	.74	23	.068	1390	.068
e....	30	9.5	.78	.78	27	.052	1860	.058
c....	30	8.3	.76	.76	45	.040	2130	.051
34 *a*....	44	4.9	.44	.48	18	.140	930	.039
b....	44	9.6	.48	.51	23	.067	1630	.034
c....	44	10.7	.51	.54	37	.047	2200	.029
d....	44	11.0	.53	.56	70	.031	3000	.023
35 *e*....	18	13.0	.75	.75	7.2	.115	1010	.070
d....	28	11.7	.67	.68	16	.063	1570	.058
c....	36	11.8	.60	.62	25	.048	2190	.044
b....	44	9.5	.49	.52	50	.035	2730	.032
a....	51	8.8	.50	.53	80	.031	3470	.024
36 *e*....	13	15.8	.38	.43	3	.115	1010	.079
d....	18	15.1	.48	.52	6.5	.076	1390	.070
c....	23	16.1	.54	.57	11	.054	1830	.060
b....	27	16.8	.54	.57	15	.044	2270	.052
a....	33	16.3	.60	.62	30	.034	3060	.038

d = distance apart of the electrodes in mm.

I = current through galvanometer in arbitrary units, proportional to the number of cathode rays per second.

D' = density of image at λ 3914 as measured by spectrophotometer.

D = density of image corrected so as to be proportional to total illumination.

t = time of exposure in minutes.

p = pressure of gas in millimeters of mercury.

V = difference of potential between electrodes in volts.

D/pIt is proportional to the light excited per collision.

is kept constant or is varied in proportion to the cathode dark space. We will consider the significance of this in just a moment.

What is the effect upon the light per collision of changing the separation of the electrodes without changing the discharge potential? To determine this we must combine the results of at least two plates. But on account of differences in development,

the absolute values of D/pIt are not comparable for different plates. For instance, $35b$ should be between $34c$ and $34d$, instead of being greater than both. By multiplying the results for plates 32, 34, 35, 36 by the arbitrary factors 0.68, 0.98, 0.77 and 0.73 respectively, however, they are all made mutually consistent. These values are plotted in Figure 2, the numbers in the circles giving the electrode separations. We see that in every case the light per collision is less, the greater the electrode separation. It should be noted that this conclusion follows directly from the

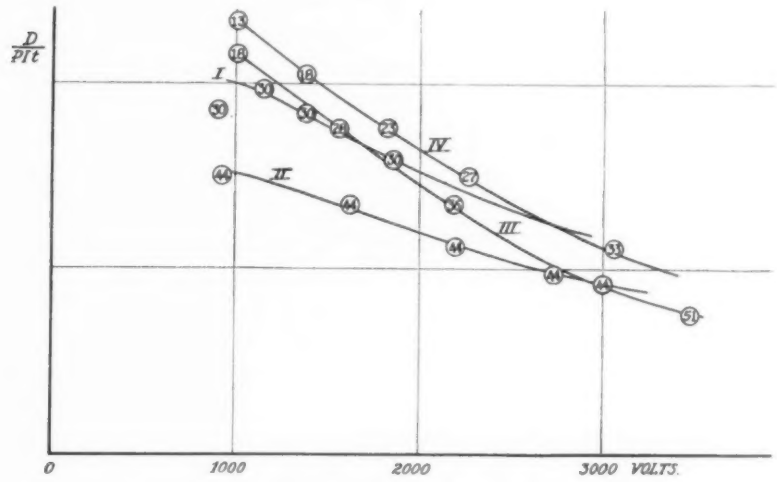

FIG. 2.—Light per collision as a function of potential difference. Numbers in circles give electrode separations.

fact that the negative slopes of the curves for plates 35, 36 are steeper than those for the plates obtained with a constant separation of the electrodes; compare $34b$ and $34d$ with $35b$ and $35d$ for instance. It does not depend on the choice of any particular values for the arbitrary factors. These were introduced merely so that the relation of the four series of observations would be properly indicated in the figure.

Now the effect of increasing the separation of the electrodes without changing the discharge potential is to increase the mean energy of the rays. This can be shown as follows. None of the

rays can come from the glow in front of the anode because the potential gradient is too small to produce rays fast enough to penetrate through the hole in the anode; and while a few may originate in the dark space, most of them must come from the region just in front of the cathode. They do not all have the same energy, however, because the potential gradient is very steep near the cathode and rays originating at different distances from the cathode will fall through different potential differences. Now the slower ones will be absorbed or retarded, as a result of collision with gas molecules, more than the faster ones; hence the mean energy of the bundle of rays will be greater, the longer the distance between electrodes; that is, for a given pressure and discharge potential. Therefore the fact that the light intensity per collision decreases as the electrode separation increases means that *faster cathode rays excite less light per centimeter of path through nitrogen at a given pressure than slower rays do.*

If we increase the voltage by decreasing the pressure, leaving the electrode separation the same, the effect of the increased voltage may be partly or wholly balanced by the effect of the decreased pressure, so that we cannot be sure whether the result would be to increase or decrease the mean energy of the rays. But if we increase the mean separation of the electrodes in proportion to the increasing length of cathode dark space, then for all voltages the number of mean free paths between cathode and anode is about the same, the absorption of rays of the same speed is also about the same, and the mean energy of the rays must be greater, the higher the voltage. But curves III and IV, Figure 2, show that under these circumstances the light per collision decreases as the voltage increases. They furnish additional evidence, then, for the conclusion that as the energy of the rays increases, the light per collision decreases.

Cathode rays, then, behave quite differently from canal rays; in one case the light excited increases with the energy of the bombardment, while in the other case it decreases. These facts help in explaining the well-known distribution of light in discharge tubes. Where there are slow electronic rays as in the positive column, or fast canal rays as in the layer just in front of the cathode,

the gas is luminous; but in the cathode dark space, since only fast cathode rays and slow canal rays pass through it, the light excited is relatively very weak.

Since the rays used in these experiments were not homogeneous, the observations do not tell us definitely the law of variation of light intensity per collision with energy. Yet they give a rough indication of what that law probably is. Compare 35*a* with 35*d*, for instance. In the first case the separation of the electrodes is nearly twice, the pressure is only half, the voltage is more than

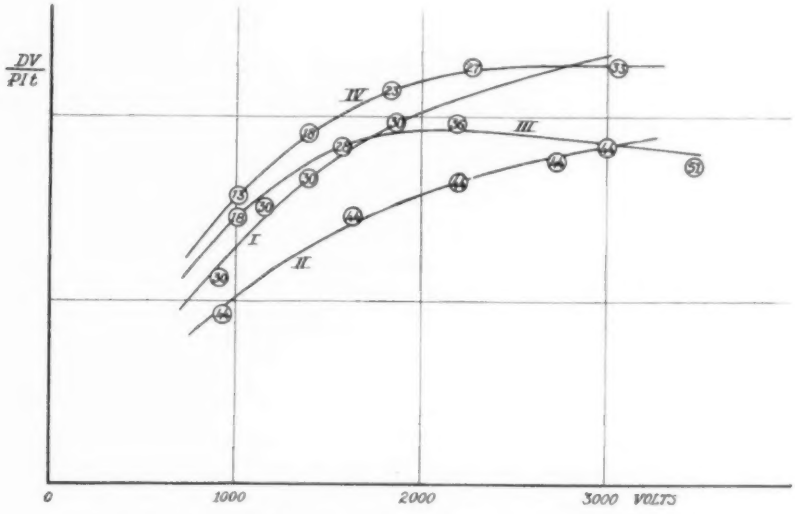

FIG. 3.—Ordinate is light per collision times potential difference

twice, and the light intensity per collision is less than half as great as in the second case. Since the dark space is the same fraction of the electrode separation in each case, it is natural to suppose that the distribution of speeds among the rays is similar in the two cases (that is, for each ray in the first case there would be one in the second case with about 0.45 as much energy), except for the effect of retardation and absorption by the gas. And since in the first case the rays are less retarded and absorbed because of their higher speeds, the mean energy of the rays in the first case should be a somewhat larger fraction of that corresponding to the dis-

charge potential than in the second case. Such considerations as these indicate that the light intensity per collision varies inversely as a power of the speed which is probably somewhat less than the second, and which seems to decrease as the speed decreases. Figure 3 strongly suggests this variation with the speed.

It is of interest to note that if we extrapolate from J. L. Glasson's[1] results for faster cathode rays we find that for the range of speeds involved here the proportion of collisions resulting in ionization is probably also inversely proportional to a power of the speed between the first and the second. If it should turn out that the light intensity per collision and the proportion of ionizing collisions each vary with the speed in the same way, then it would follow that the intensity of light per ionized gas molecule is independent of the speed of the ionizing electronic ray.

Whether this hypothesis, suggested by these experiments, is true or not can be determined only by measuring for homogeneous bundles of electronic rays both the ionization produced and the light excited per unit pressure for various speeds. I regret that circumstances have prevented me from performing the experiments indicated; and since I am not likely for some time to be in a position to continue the work, I hope someone else will undertake it.

CORNING GLASS WORKS
September 16, 1920

[1] *Phil. Mag.*, **22**, 647, 1911; cf. W. Wilson, *Proc. Roy. Soc.*, A **85**, 240, 1911.

THE VACUUM HOT-SPARK SPECTRUM OF ZINC IN THE EXTREME ULTRA-VIOLET REGION

By R. A. SAWYER

ABSTRACT

Hot-spark vacuum spectrograph for extreme ultra-violet.—After reviewing briefly the work of Schumann and Lyman, the author describes the apparatus by which spectra extending to less than 300 A were obtained. As source of light, a condensed spark was used which, it has been found, can be passed between electrodes a millimeter or less apart if sufficiently high potentials are applied, even in extreme vacuum. This source and a specially ruled, short focus, concave grating and the slit and the plate-holder, each provided with the necessary adjustments, were mounted inside a brass tube, a meter long by 15 cm. in diameter, which was kept evacuated by a diffusion pump. On account of the gas given off by the electrodes, a series of sparks lasting 5 seconds could be allowed only every 5 minutes or so, but 20 to 30 minutes' total exposure was sufficient as a rule. After precautions were taken to minimize the corrosion of the grating by active gases and also fogging due to stray light and gaseous discharge, highly satisfactory results were obtained.

Ultra-violet spectrum of zinc, 2200 to 316 A.—The wave-lengths of about 100 new lines probably due to zinc, 80 of which are below 1400 A, are given in Table I, accurate to about 0.5 A. See Plate X for spectrogram.

I. INTRODUCTION

This paper is the second of a series of articles upon the extreme ultra-violet spectra of hot sparks in vacuo. The first paper,[1] in the July number of the *Astrophysical Journal*, was concerned with the general outlines of the problem and with some special results in the case of the carbon spectrum. The purpose of the present article is to describe the details of the experiment and to present additional data on the extreme ultra-violet spectrum of zinc, supplementing preliminary results published earlier.[2] A third contribution, soon to appear, will present data on the spectra of other metals.

The problem of the extension of the spectrum into the extreme ultra-violet, that is, below 2000 angstroms, was first brought into prominence by the familiar work of Victor Schumann. In

[1] *Astrophysical Journal*, **52**, 47, 1920.

[2] *Physical Review*, **12**, 167, 1918.

the period from 1892 to 1903, using a spectrograph with optical parts wholly of fluorite and special plates of his own design, he inclosed spectrograph, plate, and source in vacuo and was able to extend the spectrum from the earlier limit to a new limit at about 1200 angstroms. The limit was imposed by the transparency of fluorite, whose principal absorption band begins at this point. The next step in the extension of the ultra-violet spectrum was made by Professor Lyman. He employed the concave grating perfected by Professor Rowland which obviated the use of both lenses and prisms and made possible a vacuum spectrograph in which there is nothing whatever in the optical path save the single reflection at the grating surface. This grating, therefore, opened the way for further extension of the spectrum, limited only by the failure of the reflecting power of the metal on which the grating was ruled, or by the lack in the source of oscillations of sufficient frequency. Availing himself of this concave grating spectrograph and using as a source a strong disruptive discharge in helium at a pressure of one or two millimeters, Professor Lyman extended the ultra-violet spectrum to 510 angstroms,[1] thus bridging more than half the gap in angstroms left by Schumann between the ultra-violet radiation of 1200 angstroms and the longest X-ray wave-lengths of about 12 angstroms.

The discharge tube as used by Lyman for gaseous or easily vaporized substances leaves little to be desired as a light source in the extreme ultra-violet. For the investigation of metallic spectra in this region, however, the lack of a suitable source of radiation has long been felt. Ultra-violet radiation is absorbed by all known gases, even at low pressures. Any successful radiator for use in the extremely short wave-lengths must be one which operates in an almost complete vacuum. Very few metallic sources are known which satisfy this requirement. The ordinary arc or spark requires prohibitive pressures. The customary procedure is to operate the arc or spark in an atmosphere of hydrogen, the most transparent gas to ultra-violet, which is separated from the evacuated spectrograph by a fluorite window. The absorption

[1] *Science*, **45**, 187, 1917; also *Spectroscopy of the Ultra-Violet* (Longmans, Green & Co., 1914).

band of fluorite then limits the spectrum to wave-lengths longer than 1250 angstroms. The only metallic source heretofore described which can be used in a high vacuum is the vacuum arc. This light was used by Saunders[1] in the ultra-violet region with considerable success, although no shorter wave-lengths have been photographed by its use than λ 977.9 for calcium. This source probably lacks sufficient energy to give rise to extremely high frequencies.

There is another metallic source upon which very little work has previously been done. It has been noted by a number of observers that when electrodes a millimeter or less apart are placed in a very high vacuum and joined to the walls of a Leyden jar to which sufficiently high potentials are applied, a short brilliant spark can be made to pass between the nearest points on the electrodes. Some years ago in the Ryerson Laboratory, Professor Millikan made a somewhat extensive study of these hot sparks in vacuo and designed and built the apparatus for the present study of their spectra. It was thought that the spectra of metals might be extended far out into the ultra-violet region, possibly beyond the limits of the extreme ultra-violet spectra previously obtained. For this hot spark seemed to fill exactly the requirements for a metallic source of extremely high frequency: it operated in the highest vacuum; any conductor sufficiently refractory to withstand the sparking could be employed as a source; the high voltages applied indicated that sufficient energy would be present to excite the highest frequencies. Work on this problem was begun in 1916 but was interrupted by war activities. The data obtained up to the time of this interruption were embodied in a preliminary report[2] and gave promise of fulfilling all expectations. Additional data since secured have fully justified the earlier hopes.

II. THE APPARATUS

Several concave gratings were ruled for the experiment at the Ryerson Laboratory. All were on speculum metal and had a radius of curvature of about 833 mm. The earliest grating had

[1] *Astrophysical Journal*, **40**, 377, 1914; **43**, 234, 1916.

[2] *Physical Review*, **12**, 167, 1918.

400 lines per millimeter. It was so damaged by the operation of causes to be spoken of later that it, like all of its successors, has had to be polished and reruled. It was reruled with 512 lines to the millimeter, giving a larger and more satisfactory dispersion. Approximately the same spacing has been used on most of the later gratings, though some have been ruled with as many as 1100 lines per mm. A compact mounting held the grating and, although occupying a cross-section hardly larger than that of the grating, permitted all necessary adjustments to be made from the rear. The spectrograph in which the grating was mounted had as its foundation a brass tube about one meter long and fifteen centimeters in diameter. This tube had flanged ends to which

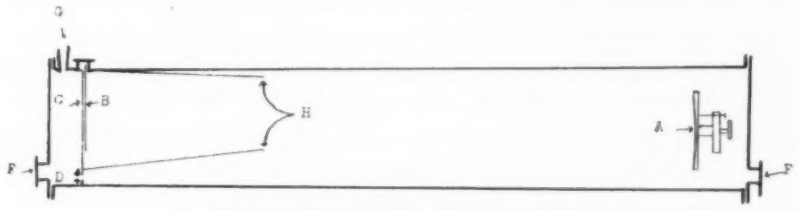

FIG. 1.—Cross-section of spectrograph

A, Grating; *B*, Plate; *C*, Diaphragm; *D*, Electrodes, represented symbolically; *E*, Slit; *F*, Windows in end plates; *G*, Connection to pump; *H*, Sleeve to keep scattered light from plates.

heavy end-plates could be screwed to make it air-tight. A plate glass window was provided in one of these end-plates and a quartz window in the other through which conditions could be observed and spark spectra taken with another spectroscope in the region of longer wave-lengths. Rubber gaskets made a seal on these ends which proved quite satisfactory.

The grating mounting was fastened at one end of this tube (see Fig. 1). About five centimeters from the other end a metal diaphragm closed the spectrograph. On the side of the diaphragm toward the grating a holder was fixed into which the photographic plate was slipped through an opening in the side of the tube. This opening, like the others, was closed by a face-plate and a rubber gasket. The photographic plate extended across about ten centimeters of the diaphragm's diameter. About two centimeters from

the end of the plate the slit was mounted in the diaphragm. The slit was adjustable in width and could be rotated in its own plane so as to make it parallel to the rulings. The lower half of the diaphragm was pierced by a two-centimeter tube to allow the main body of the spectrograph to be evacuated freely from the front end. This tube was fitted with simple light baffles at either end to render it light-tight.

The electrodes were placed just in front of the slit. They were supported by conductors which were introduced into the spectrograph through insulators, three centimeters in diameter, made air-tight by ground conical bearings smeared with rubber grease, which fitted conical openings in the wall of the spectrograph. Small electrodes of any metal could be screwed into the ends of these conductors so that different sources could be tried at will. One of the supporting conductors was free to be rotated against a ground bearing in its insulator. It was threaded at its lower end to receive a nut which bore the electrode. By rotating the conductor the nut was forced up or down and the distance between electrodes was varied. Another conical bearing was placed in the side of the spectrograph opposite the bearings for the electrodes and was ground to fit a glass joint of three centimeters' diameter, through which the tube was evacuted (see Fig. 1).

These simple arrangements comprised the original spectrograph. During the work some modifications and additions were made. These, however, were all found to be unnecessary and the final data were secured with the apparatus as described.

To secure the requisite high vacuum a Gaede molecular pump was used at first, supported by a Gaede rotary mercury pump, and that in turn by a small oil fore-pump. The molecular pump was later replaced by the Western Electric mercury diffusion pump, which was perfectly satisfactory. For the final work, however, a two-stage Westinghouse mercury diffusion pump supplanted both the Western Electric pump and the Gaede rotary mercury pump. A glass trap was placed between the pump system and the spectrograph and was immersed in liquid air at all times while the spectrograph was evacuated. In this way mercury vapor

was prevented from getting into the spectrograph and the pressure of any vapors that might be present was reduced. A McLeod gauge was attached between the trap and pumps. The gauge was calibrated to read pressures down to one ten-thousandth millimeter of mercury and would indicate pressures somewhat lower than this. During sparking, however, it not infrequently showed no reading whatever at its finest calibration mark. It is certain, therefore, that the pressure which existed in the apparatus during observations was always less than one one-thousandth of a millimeter—usually very much less.

The required potential was produced by a large induction coil, rated by the makers as a ten-inch coil. The primary of this coil was connected to a 60-cycle 110-volt alternating potential. For test exposures in air a large resistance was used in the primary circuit. To obtain the spark in vacuo, however, the full 110 volts were required. Four large navy Leyden jars connected in parallel were shunted across the secondary of the coil in parallel with the spark gap. An auxiliary spark gap in air was placed in series with the spark gap in vacuo and at the beginning of exposures was usually opened about one centimeter. As the exposure proceeded and the sparking potential rose, due to the fatigue effect,[1] this external gap was closed. These arrangements made possible a very brilliant condensed spark in vacuo; in fact, under favorable conditions the spark obtained was nearly as brilliant as the spark produced in air with an equal gap. The spark gap used in vacuo, of course, had to be very short—from 0.01 mm up to 2 mm.

The special plates perfected by Victor Schumann for work in this region of the spectrum were used. These plates were obtained from Adam Hilger and Company of London and proved perfectly satisfactory. They were developed by the pyro-gallic acid developer recommended by the makers. To prevent development fog and coarse grain on the plates, however, it was found necessary to dilute this developer one-half with water and to cool it on ice. Development on ice was found necessary by Lyman also, who,

[1] *Physical Review*, **12**, 167, 1918.

however, used an ortol-potash developer.[1] As the plates grew older, the use of potassium bromide solution to keep down fogging was found to be vital.

The grating was adjusted so that the direct image of the slit was thrown near one end or the other of the photographic plate. The dispersion of the grating was such that the whole spectral region of wave-lengths shorter than about 2100 angstroms was then obtained on the plate at once. Since the plates were not bent, it was theoretically impossible to have the entire length of the plate in exact focus. The method followed was to obtain what appeared to be a sharp focus both on the image of the slit and on the lines around 2000 angstroms. The focusing was, of course, done in air. When this adjustment had been made, the lines obtained in vacuo between the two extremes were found to be in satisfactory focus.

The zinc spectra here described were all taken with the direct image of the slit on the end of the photographic plate farthest from the slit itself. The normal of the grating then fell on the plate in the neighborhood of the 1300-angstrom region. Since all the distances involved were known, it was easy to compute the deviation from the normal of the spectrum produced under these conditions. The details of this computation and the determination of the true wave-lengths will not be entered into here. The corrections to the wave-lengths obtained by assuming a normal spectrum are found in some cases to be as much as 1.6 angstroms and have been applied to the wave-lengths here published. These corrections were not applied to the wave-lengths published in August, 1918, because the accuracy attained in their measurement did not justify such refinements. Those wave-lengths were determined simply by obtaining the grating constant by measuring carefully the distance from the slit image to some known wave-length in the region of 2000 angstroms which could be obtained in air, and assuming a true normal spectrum.

For those earlier results an accuracy of only one or two angstroms was claimed. The error of the present results cannot be greater than one-half an angstrom. This increased accuracy is due partly to the better photographs, making possible much more

[1] Lyman, *Spectroscopy of the Extreme Ultra-Violet*, pp. 130–31.

exact measurements, partly to the corrections mentioned above, and partly to the fact indicated in the preceding paper, that it was possible in the case of the carbon spectrum to check the theoretical corrections by means of short wave-length lines which appeared on the plates in the second and third order also. As a matter of fact, the corrections used should make possible an accuracy of at least two-tenths of an angstrom, and such an accuracy was obtained on the spectra of other metals, details of which will be published later; but the zinc lines, as will be noted from the photographs, are rather broad and diffuse, having a width often of three or four angstroms, and it was thought, therefore, that possibly the center of these lines was not determined more nearly than one-half an angstrom.

III. MANIPULATION AND PRELIMINARY INVESTIGATION

The process of photographing the spectrum of the spark in vacuo presented some interesting features. After the plate and electrodes had been placed in position and the spectrograph closed to the air, about an hour was required for the pumps to produce the requisite vacuum. Before any sparking was attempted, pumping was usually continued for about an hour longer to remove, as far as possible, surface layers of gas. Further preliminary pumping produced little, if any, effect. Continuous pumping during exposures was necessary to remove gases thrown off by the electrodes and insulation because of the heat of the discharge.

On throwing on the potential after two hours' pumping, a little greenish glow was observed around the electrodes. There was no general glow, however, and most of the discharge passed between the electrodes in the form of a brilliant spark, bluish white in color in the case of zinc. This discharge would so heat the electrodes, conductors, and insulation that a considerable quantity of gas would be thrown out. After the passage of three or four series of sparks, of perhaps one second in duration, the pressure in the spectrograph would be so raised by the evolved gases that the discharge would tend to become wholly gaseous. This was not allowed to happen, for the pumps would remove the gases in a few minutes and the process could then be repeated. After a number of such series

of sparks the evolved gases would be much reduced and the hot sparks became much stronger. Five or ten brilliant series of sparks of one second's duration could then be obtained at intervals of about five minutes. These intervals were necessary to allow the pumps to remove the gases which were always thrown off to some extent by the electrodes. The number of such spark series required to complete an exposure depended on the brilliancy of individual series of sparks; generally from 150 to 250 were required. As the duration of an individual series of sparks was approximately a second, it will be seen that the total period of actual exposure was not more than 15 or 20 minutes in length. Perhaps this fact, more clearly than any other, will indicate the brilliancy of the sparks obtained by this method.

The hot spark obtained with zinc electrodes was bluish white in color and very much resembled the ordinary spark in air. After a few poor sparks at the beginning of an exposure, the sparks attained a maximum of brilliancy which gradually fell away as the fatigue effect, previously mentioned, became operative. This effect became more and more pronounced and made the sparks more and more difficult to produce. The electrodes spattered badly and their tips began to present a rough and fused appearance. This fatiguing had been previously studied at great length by R. A. Millikan and has been briefly reported upon.[1] It actually in some instances imposed a limit on the length of exposure, so difficult did it become to get anything across the gap, even when this was reduced to a tenth of a millimeter.

The early photographs taken as described were found to be badly fogged. Part of the fogging was thought to be due to the general glow in the tube produced by the discharge in the quantities of gases driven out by the first sparks. A shutter, therefore, was placed in the tube just back of the diaphragm. This shutter was operated from outside the spectrograph by a powerful magnet. Investigation showed that no amount of glow in the front end of the tube affected the plate when this shutter was closed. It did not stop the fogging during exposure, however, and further investigation was made of the cause. On the supposition that it might be due to

[1] *Physical Review*, **15**, 239, 1920.

scattered light reflected from the sides of the tube and the grating, the blackening of the interior of the tube was made more perfect and various systems of diaphragms and shields were tried. The shielding device which was finally used was a tin sleeve 25 cm long, fastened to the diaphragm. This sleeve not only completely shielded the plate from light from the sides of the tube but, after the opening at the far end was adjusted, permitted light from the ruled part of the grating only to fall on the plate. When this sleeve was used, fogging was greatly reduced. A little always remained and the plates at the best have never been wholly clear, though whether the residuum is a light fog or one due to chemical processes in the development is not certain. Indeed, it is very difficult to distinguish between these two effects.

A more serious difficulty was met in eliminating the cause of a corrosion which was noticed on the grating. This corrosion was sufficient to cause marked discoloration of a new grating in a single exposure and to diminish its power so that a few exposures rendered it useless. This situation made it impossible to get the best results from a grating, even for a single exposure, and considerable time was spent in seeking the cause. From the fact that much of the discoloration could be removed by wiping the grating with a bit of absorbent cotton moistened with a mixture of alcohol and ether, it was thought that the corrosion might be largely physical, caused by spattered particles shot off from the spark. To test this possibility a pair of condenser plates were mounted just behind the slit with faces parallel to the light beam. This condenser was charged during sparking to 1000 volts per millimeter by a large storage battery. Very little material was caught on the plates, however, and the corrosion still persisted. To see, then, if the effect was purely chemical, small mirrors of polished copper were placed in the spectrograph entirely out of the path of the light beam. These mirrors became more heavily corroded than the speculum metal gratings. Indeed, sufficient corrosion accumulated for chemical analysis, which showed that the corrosion was a sulphide, produced, apparently, by the free sulphur and sulphur compounds present in the hard rubber insulation and rubber gaskets. The hard rubber insulation of the electrode-bearing

conductors was replaced by redmanol or synthetic amber, produced by the Redmanol Chemical Products Company of Chicago, and the gasket rubber was replaced by sulphur-free antimony-cured gasket rubber kindly supplied by Dr. Grafton, of the Manhattan Rubber Company of New Jersey.

These changes made a great improvement. Not only was the corrosion markedly reduced and the life of the grating lengthened in consequence, but very much less gas was thrown off during sparking, longer series of sparks became possible, and a better vacuum was maintained. A result of the better vacuum was the reduction of the fogging caused by glow in the tube, and much clearer photographs were obtained. There still remained a slow corrosion of the grating due probably to very active gases, possibly higher nitrites given off by the electrodes themselves, since these are known to be produced in great quantities by arcs and sparks in air. Frequent renewals of the grating, therefore, were still necessary, but conditions were much better than those which had existed earlier, and the extreme ultra-violet spectra which had long been hoped for were now obtained.

IV. RESULTS

A typical zinc spectrum obtained under the conditions described is shown in Plate X, *a* and *b*. A plate exactly as obtained is shown at *a*, while *b* shows it magnified laterally, much as stellar spectra are magnified. The lines on the original plate are necessarily short because of the short spark-gap. The slight fogging described renders the background somewhat cloudy. The lines, however, are definite enough to be easily measured by a comparator. They were measured by a Gaertner comparator and the wave-lengths determined as stated above. Table I gives the wave-lengths obtained with their relative intensities. A few other observers have worked on the ultra-violet spectrum of zinc, obtaining in some cases lines of as short wave-length as λ 1450. Such of their lines as seem to coincide with the results of this work are included in the tables. Handke's and Wolff's wave-lengths are taken from Lyman's *Spectroscopy of the Ultra-Violet*, page 123.

TABLE I

ULTRA-VIOLET SPECTRUM OF ZINC

Wave-Length*	Intensity	Character†	Handke Spark	Wolff Arc	McLennan, Ainslie, and Fuller Arc in Vacuo	Saunders' Vacuum Arc
316.4	0					
319.7	0					
322.8	0					
336.0	0					
340.1	0					
342.9	0					
424.9	0					
427.8	1					
430.5	1					
433.3	0					
435.7	0					
437.5	0					
441.5	0					
443.8	1					
446.4	0					
449.4	1					
452.0	1					
455.8	0					
458.5	0	Carbon ?				
467.3	2	Double				
472.8	2	Double				
477.7	1					
480.7	0					
502.2	0	Double				
507.6	0	Double				
573.9	1	Carbon				
641.5	0	Carbon				
677.9	5	Double				
703.7	1	Carbon ?				
714.0	0					
755.4	0					
767.4	1					
779.6	0					
788.8	0					
802.8	0					
812.5	1					
825.0	1					
833.5	3	Carbon				
844.7	0					
851.5	1					
860.9	1					
871.7	0					
881.4	0					
887.5	0					
898.2	1					
903.6	2	Carbon				
912.0	0					
921.3	0					
927.1	0					

* Wave-lengths reduced to vacuum.
† "Carbon" indicates line probably due to carbon.

TABLE I—*Continued*

Wave-Length*	Intensity	Character†	Handke Spark	Wolff Arc	McLennan, Ainslie, and Fuller Arc in Vacuo	Saunders' Vacuum Arc
935.5	0	Double Carbon?				
945.7	1					
950.2	1					
957.7	1					
965.2	1					
976.9	3	Carbon				
989.9	3					
1001.2	3					
1009.3	3	Carbon				
1017.6	3					
1023.2	2					
1029.8	2					
1036.1	3	Carbon				
1043.4	2					
1048.8	3					
1066.3	2	Triple Carbon				
1080.5	1					
1085.1	1					
1094.2	1					
1102.2	1					
1109.5	1					
1117.0	1					
1135.6	1	Double				
1145.5	1					
1155.9	1					
1165.9	1					
1176.6	1	Carbon				
1186.6	1					
1194.6	0	Carbon?				
1201.5	1					
1215.9	1	Hydrogen				
1223.1	1					
1228.6	1					
1252.5	0					
1264.0	0					
1273.1	0					
1282.9	0					
1293.3	0					
1306.1	0					
1320.1	0					
1330.5	0					
1342.8	0					
1376.7	0					
1451.1	0			1450.8	1451.1	
1456.8	0			1457.6	1457.5	
1464.3	0					
1473.5	0			1474.7		
1478.5	0					
1485.6	0			1486.2	1486.2	
1499.5	0					
1505.8	0					
1515.9	0					

TABLE I—*Continued*

Wave-Length*	Intensity	Character †	Handke Spark	Wolff Arc	McLennan, Ainslie, and Fuller Arc in Vacuo	Saunders' Vacuum Arc
1552.2	1	.....	.....	.....	.....	.....
1561.1	1	Carbon	.....	.....	.....	.....
1581.4	2	.....	.....	.....	.....	.....
1598.1	2	.....	.....	.....	.....	.....
1601.4	2	.....	.....	.....	.....	.....
1619.6	2	.....	.....	.....	.....	.....
1622.8	2	.....	.....	.....	.....	.....
1629.3	3	.....	.....	.....	.....	.....
1639.1	2	.....	.....	.....	.....	.....
1644.7	2	.....	1647.0	.....	.....	.....
1651.5	2	.....	1653.2	1649.9	.....	.....
1672.7	3	.....	1673.6	.....	.....	1673.1
1688.5	2	.....	1689.0	.....	.....	1689.0
1695.4	1	.....	1695.9	.....	.....	.....
1706.3	2	.....	1707.0	.....	.....	1706.9
1749.4	3	.....	1750.4	.....	.....	1749.6
1753.4	1	.....	1754.1	.....	.....	.....
1761.7	0	.....	.....	.....	.....	.....
1767.5	2	.....	1768.0	.....	.....	1767.8
1811.0	1	.....	1811.2	.....	.....	.....
1833.3	1	.....	1834.0	.....	.....	1833.8
1838.8	2	.....	1839.8	.....	.....	1839.2
1856.3	1	.....	.....	.....	.....	.....
1864.4	2	.....	1864.6	.....	.....	.....
1919.6	1	.....	1919.5	.....	.....	1919.0
1930.0	1	.....	1931.2	.....	.....	.....
1953.5	1	.....	1953.1	.....	.....	.....
1982.2	1	.....	1982.7	.....	.....	1982.2
2025.7	20	.....	.....	.....	.....	.....
2062.8	20	.....	.....	.....	.....	.....
2101.0	5	.....	.....	.....	.....	.....
2139.2	3	.....	.....	.....	.....	.....

Saunders' complete results are in the *Astrophysical Journal* (**40,** 377, 1914), while McLennan, Ainslie, and Fuller's work is published in the *Proceedings of the Royal Society of Canada* (**95,** 316, 1919). Wave-lengths 2026.1, 2100.6, and 2139.2 were taken as standards. The values are those of Kayser's *Handbuch der Spectroscopie*, **6,** 1033, reduced to vacuum.

The lines here given coincide well with those published in August, 1918, with the exception of the region 1250–1450 angstroms. On the later plates, several of the lines in this region, and a few other lines, as well, while undoubtedly present, were too weak for measurement on the comparator. The earlier measurements were made with a steel rule and the naked eye and much fainter lines were, therefore, included.

The zinc used for electrodes was chemically pure and it is believed that most of the lines are true zinc lines. A few lines, however, are thought to be due to carbon, as indicated in the table, and λ 1215.9 is assigned to hydrogen. These are the lines as described in the preceding paper which appear on all the plates except those taken with chemically pure silver, which has only the hydrogen line and possibly one more.

The spectrum of zinc, then, is extended to 316.4 angstroms. There can be little uncertainty about the reality of practically all the lines, since most of them have been obtained with different gratings. The position of the group of lines of shortest wave-length is marked in Plate X, *b* and it is hoped they can be seen. The group around 430 angstroms will certainly be apparent. It is interesting to note that the spectrum seems to cease rather abruptly at 316.4 angstroms, for the same grating shows that the iron spectrum extends still farther down.

Clearly the two most important factors in the solution of this problem were a very high vacuum, without which no sparks could be obtained, and a satisfactory grating. For work in the extreme ultra-violet the character of the grating is of the highest importance. Since work is done in the first order spectrum only, the largest part of the light must be thrown into this order. The extreme shortness of wave-length in comparison with grating space necessitates a high uniformity of ruling. Since the appearance of the visible spectrum seems to give little, if any, indication of the value of the grating for the ultra-violet, the earlier gratings were good largely by chance. Great improvement has been effected in the later gratings by the methods described in Professor Millikan's paper which preceded this, though the corrosion of the grating still necessitates frequent renewals.

UNIVERSITY OF CHICAGO
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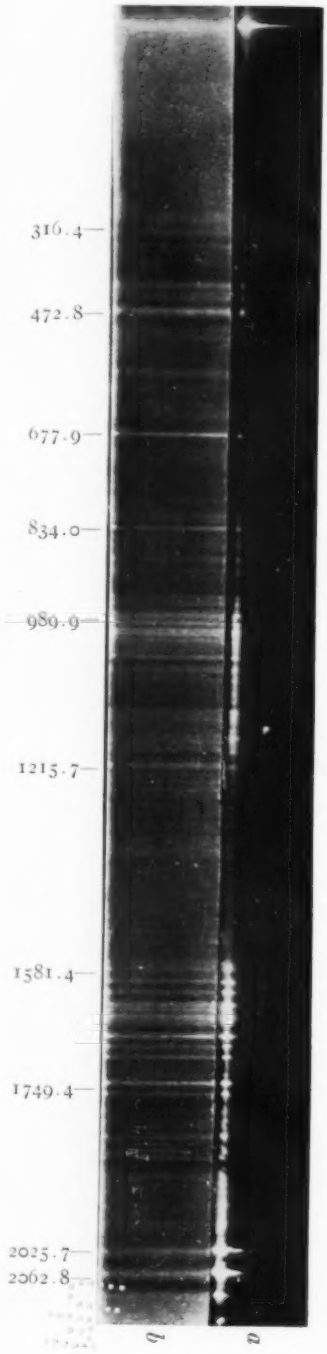

PLATE X

THE SPECTRA OF SOME COMPOUND GASES IN VACUUM TUBES

By W. H. BAIR

ABSTRACT

Band spectra of six compound gases, in visible and ultra-violet regions.—Ammonia, nitrous oxide, nitrogen peroxide, carbon dioxide, hydrogen sulphide, and sulphur dioxide were excited in an ordinary discharge tube, both with the gas flowing and at rest, and spectrograms were secured with a three-prism glass spectrograph and with a small quartz spectrograph. The ammonia band in the visible spectrum has two heads, each degraded on both sides. The band at λ 3371 is very probably not due to ammonia, as it is found in tubes long after the characteristic color of ammonia has disappeared. Both oxides of nitrogen show strongly the *third positive group of nitrogen bands*, especially with the flowing gas. This group of bands was observed from λ 3458 to λ 1902; those at the more refrangible end appear not to follow Deslandres' law. Of the *two negative groups of carbon bands*, the first is probably due to carbon monoxide and the second to carbon dioxide. Several new bands were observed in this second group, and forty new bands were discovered in the spectrum of sulphur dioxide, extending this group to λ 2124.

This paper is a report of work done on the spectra of some compound gases as given in discharge tubes. The usual readiness with which such gases decompose when an electric discharge is passed through them is, as is well known, the chief difficulty encountered in such work. The usual way of overcoming this is to pass the discharge through flowing gas, thus replacing the decomposed gas as rapidly as is necessary by a fresh supply. This method was followed in the present work. For purposes of comparison, the apparatus was so constructed that the gas could be readily studied at rest also.

APPARATUS

Discharge tubes, varying in diameter from 4 to 6 mm and in length from 15 to 20 cm were employed in the usual end-on position. One end of the tube was closed with a quartz window for work in the ultra-violet. The tube was exhausted by means of a Gaede mercury pump in series with an oil pump. The gas to be studied entered the discharge tube through a capillary tube, which was 80 cm long and about 0.15 mm in diameter. At the end of the

capillary farther from the discharge tube, there was an adjustable cistern of mercury, which was used to regulate the rate of flow of gas into the discharge tube. A stopcock between the capillary and the discharge tube served to shut off the gas supply whenever it was desired to study the gas at rest.

The electrical discharge was produced by a one-kilowat Thordarson transformer, operated on a sixty-cycle alternating current. The intensity of the discharge could be varied by a magnetic shunt and by series resistance in the primary. The discharge entered the tube through aluminum electrodes, which were fastened in the tube with red sealing wax.

Spectrograms of the visible region were obtained with a three-prism glass spectrograph, which transmitted to about λ 3800 and gave a dispersion of about 5 A per mm in this region. For work in the ultra-violet, a small single-prism quartz spectrograph was used. It gave a dispersion of about 15 A per mm for λ 2500. Seed "L-Ortho" dry plates were used in both spectrographs.

The gases studied were ammonia, nitrous oxide, nitrogen peroxide, carbon dioxide, hydrogen sulphide, and sulphur dioxide.

AMMONIA

As is generally known, two bands, one in the green-yellow and one in the ultra-violet, are usually attributed to ammonia. However, the behavior of these two bands differs greatly with varying conditions. Thus, with flowing ammonia gas, the band in the visible region is strong; but it disappears almost immediately if the supply of fresh gas is cut off. The band in the ultra-violet, on the other hand, continues indefinitely in the gas at rest. E. P. Lewis[1] has shown that it is given by mixtures of nitrogen and hydrogen, through which the discharge has passed for hours. A study of this gas was undertaken in the hope that further information might be secured concerning the origin and behavior of these bands.

For this purpose, commercial ammonia gas was used. It gave the usual greenish-yellow color when flowing and the rose color of nitrogen when at rest. A photograph of the visible band was

[1] *Astrophysical Journal*, **40**, 154, 1914.

obtained with the glass spectrograph. This was rather difficult as the band falls in that part of the spectrum to which photographic plates are not very sensitive. Wratten and Wainwright panchromatic plates were tried without success, and finally an exposure of forty-five hours with an L-Ortho Seed plate, gave a fairly satisfactory negative.

Besides the ammonia band, the plate showed very faintly some of the stronger band heads of the second positive nitrogen group in the blue and violet. The ammonia band, as Lecoq[1] showed, consists of two heads, having their maximum intensities 60 or 70 A apart, the more intense of the two being on the side of shorter wave-lengths. This is also the case with the band in the ultra-violet, as is shown by exposures made with the quartz spectrograph, and as the spectrograms of Fowler and Gregory[2] also show. Both heads shade off on either side of their maximum intensities, being shorter on their adjacent sides. On their outer sides, the more refrangible band is the longer. Their extreme limits are indeterminate, due to their faintness and to the fogging of the plates. However, they seem to cover a region 250 to 300 A in extent. No further structure of the bands was observable with the dispersion used. Capacity, self-induction, and the spark gap had no visible effect on the band. That the band in the visible region is double can be seen with a Hilger's direct-vision spectroscope, as was observed after the spectrogram had revealed the fact.

Spectrograms obtained with the quartz spectograph for the ordinary discharge in ammonia show the ultra-violet band at λ 3371 when the gas is flowing, but not when it is at rest. The insertion of a small capacity and an inductance brought out this band strongly in the gas at rest, but had no appreciable effect on the moving gas. Exposures under these conditions show the ultra-violet band two or three times as intense with the gas at rest as with it moving. Thus, while the visible band disappears almost instantly on stopping the flow of gas, the one in the ultra-violet may be made more intense under the same conditions by insertion of capacity and inductance in the circuit. Mixtures of flowing

[1] *Comptes Rendus*, **69**, 1189, 1869.

[2] *Phil. Trans.*, Ser. A, **218**, 351, 1919.

ammonia and oxygen gave the ultra-violet band with the uncondensed discharge. Accordingly, the origin of this band still seems to be in doubt, though the present work appears to strengthen Lewis' suggestion that it may be due to a compound of nitrogen and hydrogen, which is more stable than ammonia.

It may be noted also that the third positive group of nitrogen bands was absent from all photographs of ammonia gas. No trace of even the strongest bands of this group was found on any of the plates, with exposures made either with the gas flowing or at rest, except in the cases where oxygen had been added. Beyond the limits of the second nitrogen group only the continuous spectrum of hydrogen was present, with an occasional mercury line. This continuous spectrum was strong with the gas at rest. It fell off rapidly in intensity beyond λ 2200, disappearing entirely at about λ 2100. If the continuous spectrum of hydrogen exists at all beyond λ 2100 under conditions here studied, it must be very feeble, as the quartz system used transmits readily to λ 1950. Capacity and self-induction had no appreciable effect on the intensity of this spectrum.

NITROUS OXIDE

Commercial nitrous oxide, obtained from the French Oxygen Company of Oakland, was used in these experiments. A discharge, passing through the flowing gas, gave a roselike color, surrounded by a greenish phosphorescence. The green color was much stronger in side tubes than in the direct path of the discharge. It disappeared in a few seconds from all parts of the tube, on stopping the flow of the gas. The phosphorescence was much fainter with nitrous oxide than with nitrogen peroxide. Throughout the visible region, the flowing gas showed a continuous spectrum, with its maximum intensity in the green and yellow. The bright bands, reported by Gehlhoff,[1] were observed in the red and yellow. The second positive group of nitrogen bands appeared in the blue and violet.

Photographs with the quartz spectrograph show the second and third positive groups of nitrogen, both with the gas flowing and at

[1] *Annalen der Physik*, **24**, 553, 1907.

rest, the third group being relatively more intense with the flowing gas. As this advantage is still more pronounced with nitrogen peroxide, a discussion of the third group is deferred until that gas is considered. Attention should be called, however, to one exposure made with flowing gas and with a small capacity and a spark gap in the circuit. This exposure shows two very strong band heads at λ 2188 and λ 2119, with a third weaker one at λ 2050. These bands have the structure of bands of the third group. The band at λ 2156 was also much reduced in intensity. A number of attempts to reproduce these bands failed, though the conditions of the former exposure were reproduced as nearly as possible. Accordingly, the exact condition for their reproduction remains unknown. Their intensities suggest that they might belong to the first series of this group, and in this region no first series bands have been reported. However, their wave-numbers do not correspond with values given by Deslandres' law. The validity of this law in the more refrangible end of this group is further considered in connection with results obtained with nitrogen peroxide.

NITROGEN PEROXIDE

To prepare nitrogen peroxide, chemically pure lead nitrate was heated in a test tube with a Bunsen flame. The liberated gas was passed through a P_2O_5 tube and then condensed in a cooling tube, immersed in a mixture of salt and ice. This tube was then joined to the discharge tube by means of the long capillary tube and the rate of flow of the gas regulated by varying the temperature of the liquid nitrogen peroxide.

The electric discharge through the flowing gas gave the characteristic greenish color throughout most of the tube. For slowly moving gas the end nearer the exit gave the color of nitrogen; for rapidly moving gas, this was replaced by the greenish yellow, and at the entrance there was a pinkish tint. Only once, and then for just a few seconds, did the yellow color described by Zenneck and Strasser[1] appear at the entrance. The conditions for its reproduction were not determined. When the flow of gas was stopped the rose color of nitrogen slowly filled the tube. Side

[1] *Physikalische Zeitschrift*, **12**, 1201, 1911.

tubes showed the greenish-yellow color for as much as five minutes after the supply of fresh gas was cut off. When viewed with a hand spectroscope, the flowing gas showed the strong lines reported by Gehlhoff, a strong continuous spectrum in the yellow and green, and the second positive group of nitrogen in the blue and violet. Thus, the general appearance of the visible radiation with this gas is very similar to that obtained with N_2O, except that the phosphorescent effect is much more intense with the former, and accordingly a corresponding increase in the intensity of the continuous radiation in the yellow and green occurs.

A number of photographs of the spectrum of the gas, both flowing and at rest, were secured with the quartz spectrograph. Both the rate of flow of the gas and the density of the electric discharge were varied through wide ranges. In all cases, the second and the third group of nitrogen bands appeared. With the flowing gas, however, the second group of bands was much weaker than with the gas at rest. Reduced density of electric discharge increased this effect. This decrease in intensity was not uniform throughout the group, the bands of the fourth and fifth series suffering a greater diminution in intensity than those of the other series.

The third group of bands, on the other hand, was slightly more intense with the flowing gas, which offered better conditions for the study of this group. A number of new bands were discovered, thus extending this group in both directions several hundred angstroms beyond its present limits. Most of the new bands in the extreme ultra-violet were very weak and an accompanying continuous radiation made it difficult to secure spectrograms satisfactory for wave-length determinations. The best conditions for photographing this region were found to be secured with a feeble electrical discharge and the gas flowing at such a rate as just to allow the discharge to pass readily.

Measurements of all observed bands were made and the wave-lengths calculated by use of the Hartmann formula. The results are given in Tables I and II. Table I contains only bands of the third positive group of nitrogen. For comparison, Deslandres' results are also given. A glance at the first and fifth columns

TABLE I

Third Positive Group of Nitrogen

Present Results				Deslandres' Results			
λ	$1/\lambda\ 10^7$	d_1	d_2	λ	$1/\lambda\ 10^7$	d_1	d_2
3458.0	2891.9						
3375.0	2963.						
3302.5	3028.0						
3278.0	3050.6						
3200.6	3124.4						
3120.2	3204.9						
3170.3	3154.3						
3112.0	3213.4						
3043.9	3285.3						
2984.0	3351.2						
3008.2	3324.2	169.9		3007.2	3325.4		
2949.2	3390.9						
2898.0	3450.7			2896.2	3452.8		
2849.0	3510.0		3.1				
2859.4	3497.2	173.0		2857.9	3499.1	173.7	
2810.0	3558.7			2809.2	3559.7		
2762.9	3619.4			2762.7	3619.6		
2735.5	3655.6		3.8				1.4
2721.8	3674.0	176.8		2721.7	3674.2	175.1	
2679.2	3732.5			2679.5	3732.0		
2638.5	3790.0			2638.8	3789.6		
2610.4	3830.8		3.3	2610.6	3830.5		2.6
2595.3	3853.1	179.1		2596.1	3851.9	177.7	
2558.3	3908.9			2558.9	3907.9		
2525.0	3960.4			2524.8	3960.7		
2497.1	4004.7		2.6	2499.0	4001.6		4.3
2478.4	4034.8	181.7		2479.0	4033.9	182.0	
2446.8	4087.0			2446.9	4086.8		
2425.5	2122.9			2416.9	4137.5		
2384.8	4193.2		2.4				3.0
2370.3	4218.9	184.1		2370.3	4218.9	185.0	
2330.0	4291.8						
2315.8	4318.2			2315.7	4318.3		
2288.7	4369.3		5.0	2289.2	4368.3		5.1
2268.6	4408.0	189.1		2268.1	4409.0	190.1	
2244.1	4456.1			2244.3	4455.7		
2221.1	4502.3			2222.1	4500.2		
2198.3	4549.0		−11.4				
2180.7	4585.7	177.7					
2156.6	4636.9			2154.1	4642.3		
2134.1	4685.2						
2115.0	4728.1		.3				
2099.2	4763.7	178.0					
2078.4	4811.4						
2060.0	4854.4						
2034.7	4914.7		5.8				
2021.4	4947.5	183.8					
2003.0	4992.4						
1983.8	5040.8						
1960.9	5099.7		−11.0				
1953.0	5120.3	172.8					
1934.9	5168.2						
1923.0	5200.2						
1907.0	5245.9						
1902							

serves to make clear the new bands and the extended limits of this group. Table II contains only unidentified bands.

TABLE II

UNIDENTIFIED BANDS

λ	λ	λ
3883.8	2919.9	2207.3
3869.1	2713.0	2188.3
3658.3	2497. \ Number of bands	2140.
3649.3	2478. ∫ between these	2119.
3029.6	2391.7	2050.
2957.6	2299.7 \ Number of bands	2021.4
2927.6	2268. ∫ in this region	

The four heads in each subgroup have been described as diminishing in intensity from the first to the fourth. The relative intensities of these heads, however, vary greatly from group to group. Thus, in the groups with the first bands at λ 2859 and λ 2722 the second and third heads are almost of the same intensity as the first. The group beginning at λ 2596 has the second head almost as strong as the first; but the third has weakened until comparable in intensity with the fourth. Of the new groups discovered beyond λ 2200, the two with their first heads at λ 2180 and λ 2099 have the first band heads less intense than the second and third. At the less refrangible end of the group, it is difficult to make intensity comparisons, owing to the overlapping of the second group. It seems clear, however, that the second and third heads are at least of equal intensity with the first. The fact that in each of the two last groups in this end of the spectrum the first head has not been detected may be due to its diminished intensity. Calculations based on the assumption of Deslandres' law show that they should fall on comparatively clear places between bands of the second group. Accordingly, if they exist at all, they must be much weaker than the second and third heads of their respective groups. The only new first series band found in this region, namely, λ 3170, is less intense than the other bands of the group.

Throughout the whole range of the third group, a number of unidentified bands were measured, the results being recorded in Table II. These are most numerous in the regions of the third

and fourth bands in the groups beginning at λ 2478 and λ 2370. Some of them lie close to bands of the third group and have very much the appearance of third subheads of these bands, as at λ 2425, λ 2385, and others. Mostly, however, they suggest no connection with the third group. Other irregularities observed in the two groups mentioned above are the shifting of the head at λ 2330 from what should be its location toward the third head of the group, and the variations in intensity of the band at λ 2425. This band, though weaker than others of the group, is distinct with the flowing gas, but disappears entirely from some photographs taken with the gas at rest.

The second differences (d_2) for the wave-numbers of the first series as given in Table I are seen to be not even approximately constant beyond λ 2268. The same is true of other series, except that on the more refrangible side of λ 2268 they are less regular than series one. This is partly due to the less accurate wave-length determinations and partly to evident displacement of bands, as mentioned above. A plot of the wave-numbers of the entire group shows regular arrangement in general, except for such irregularities as occur at λ 2330. When compared, however, with the plot of values calculated by use of Deslandres' formula, a crowding together of the subgroups in the extreme ultra-violet is observed. That is, the wave-numbers from observation do not increase in this region so rapidly as do those calculated by use of the formula. The fact that the second band (λ 2156) in the group beginning at λ 2180 is stronger than the first suggests that it may belong to the first series. But as Schneiderjost[1] has pointed out, it does not fit into this series.

The foregoing facts may indicate that Deslandres' law is not followed in the extreme ultra-violet of the third group. This law is a first approximation, and other variations from it in long series have been reported. This explanation, however, does not take account of the three bands found on one exposure made with nitrous oxide. A second possible explanation is that we have here the beginning of a new group of bands. Some plates gave indications of bands beyond those recorded in the table; but their presence

[1] *Zeitschrift für wissenschaftliche Photographie*, **2**, 265, 1904.

was made uncertain by their faintness and the fogging of the plate by scattered radiation. However, the structure of these bands favors considering them as members of the third group. Further work is needed to decide between these possibilities.

CARBON DIOXIDE

Commercial carbon dioxide was used in these experiments. With the gas flowing rapidly, there appeared a faint red color, which extended a centimeter or two from the point at which the gas entered the tube. This color disappeared almost instantaneously on stopping the flow of gas, leaving the tube white throughout. The hand spectroscope showed the positive bands with equal intensity with the gas flowing and at rest. Spectrograms secured with the quartz spectrograph show the third and fourth positive groups in the ultra-violet. No relative difference between the intensities of the groups was observed with the gas flowing and at rest. Some exposures with the gas at rest, however, showed a continuous radiation, which is due perhaps to hydrogen. Capacity and self-induction had no effect except to vary uniformly the intensity of the radiation.

Wave-length determinations for bands of the third group were not made, but the band, reported by Deslandres at λ 2295, and which Hof[1] failed to observe, was found on all plates. Hof also found no bands of the fourth positive group beyond λ 2215. As this group was found to extend even beyond the limits given by Deslandres[2] measurements were made of the bands in its more refrangible end. The values are recorded in Table III and serve to identify them as the bands reported by Deslandres. Values beyond λ 2000 are only approximate, as they lie beyond the limits of the zinc spark, which furnished the comparison spectrum and had to be determined by extrapolation. They evidently represent some of the more intense of the bands reported by Lyman[3] in his work on the extreme ultra-violet.

[1] Inaugural dissertation. Leipzig: Barth, 1914.

[2] *Comptes Rendus*, **107**, 842, 1888.

[3] *Spectroscopy of the Extreme Ultra-Violet* (Longmans, Green & Co, 1914).

With flowing carbon dioxide, a violet sheath appeared around the electrode nearer the entrance of the gas. This color disappeared soon after the supply of gas was shut off. With rapidly flowing gas, that is, with higher pressure, it lasted as long as twenty to twenty-five seconds after the supply of gas was stopped; with lower pressures, it vanished within approximately ten seconds after the gas supply was cut off. Spectrograms obtained with the quartz spectrograph as the gas flowed by the electrodes showed both the first and second negative groups. Their relative intensi-

TABLE III

FOURTH POSITIVE GROUP OF CARBON

λ	λ	λ (Lyman)
2262.6	2112.8	.....
2247.5	2107.7	.....
2238.6	2089.4	.....
2222.1	2067.3	2068.4
2216.3	2046.1	2047.0
2196.9	.....	2035.1
2189.3	2031.4	2031.7
2188.	2026.	2026.4
2173.5	2012.5	2012.6
2150.4	2007.6	2007.2
2128.4	1990.	1991.0
.....	1967.7	1970.1
.....	1946.2	1953.0
.....	.....	1951.7
.....	.....	1950.4
.....	.....	1933.6

ties varied greatly with the conditions of the discharge. The second group was strongest with the gas flowing rapidly and with the electrical discharge weak. Capacity and self-induction diminished its intensity. The group appeared on exposures made with the gas at rest, but the intensity was greatly diminished, and with lower pressures only the more intense of the bands were distinct, the positive group supplanting most of them. The first negative group, on the other hand, showed only faintly the stronger bands with the rapidly flowing gas and was most intense with the gas at rest and the pressure low.

Besides the bands of the second group, which are given by Deslandres, there is, on the side of the shorter wave-lengths, one at λ 3155 and one at λ 3030.

On the side of longer wave-lengths, there are band heads at λ 4125, λ 4340, λ 4450. These values are only approximations, owing to the small dispersion of the spectrograph in this region. Beyond these are other ill-defined bands, which probably belong to the second group, as they are intense on exposures made with the flowing gas and very weak when the gas is at rest. An attempt was made to photograph this region with the glass spectrograph, but owing to the greater dispersion an exposure of forty-five hours gave results too faint for measurements. The exposure showed, in addition to numerous lines and bands of the positive group, indications of bands degraded toward the red. A much longer exposure is required to give definite information concerning this region.

From the foregoing results it seems probable that the two negative carbon groups are due to different emission centers. Since the second group is very much stronger with the flowing gas than with the gas at rest, one seems justified in attributing it to carbon dioxide. The first group is probably due to some other compound, perhaps CO, formed by the decomposition of CO_2. According to Hof, it appears with equal intensity in CO and CO_2.

SULPHUR COMPOUNDS

Hydrogen sulphide was prepared from iron sulphide and sulphuric acid and dried in a P_2O_5 tube. A discharge through the flowing gas gave a blue color in the tube and the hand spectroscope showed bands degraded toward the red. With the gas at rest, the color of the tube quickly changed to red, probably due to hydrogen, as the hydrogen C-line showed strongly in the spectroscope. The gas decomposed rapidly, even with the feeblest possible discharge passing, depositing sulphur on the walls of the tube. With a heavier discharge, numerous globules of sulphur were formed in the tube, even in the direct path of the discharge. Films soon formed on the windows of the tube, thus reducing the intensity of the radiation, especially in the ultra-violet. However, satisfactory spectrograms were obtained with the glass spectro-

graph, and one not so good with the quartz spectrograph. These plates showed a number of bands degraded toward the red and extending to about λ 2800. Their identity as sulphur bands was established by comparison with the emission spectrum of that element, as given in the *Atlas* of Hagenbach and Konen.

Sulphur dioxide, being a more stable compound than hydrogen sulphide was substituted for the latter. It was prepared by heating concentrated sulphuric acid with metallic copper. The gas was then dried in a P_2O_5 tube and collected over mercury.

An electric discharge through the flowing sulphur dioxide gave a blue color in the tube, which did not change appreciably on stopping the flow of the gas. Sometimes with the flowing gas a greenish-yellow sheath appeared around the electrodes. As the discharge continued to pass, a thin film of sulphur was deposited in the cooler parts of the tube. The amount of sulphur deposited, however, was in no case comparable with the deposit from hydrogen sulphide. The hand spectroscope showed a continuous spectrum throughout the visible region. A few bands degraded toward the red showed indistinctly through this continuous background.

Spectrograms secured, both with the gas flowing and at rest, show a group of bands extending to λ 2225. The continuous radiation observed in the visible spectrum is strong to approximately λ 3000, being more intense with the gas at rest. Most of the bands observed are degraded toward the red, and, with the instrument used, are not resolved into lines. No sharp line, such as is found with bands of nitrogen and carbon, marks the head of these bands. The termination of a band on its more refrangible side is indicated by an abrupt change in the intensity of the radiation. Between λ 3160 and λ 2860 the bands are more numerous than in other parts of the group; most of them, however, have no definite heads, but shade off indefinitely on both sides. The general appearance of this region is distinctly different from the rest of the spectrogram and strongly suggests another group of bands, superimposed on the group which has the definite heads. The average range of these bands is from 10 to 15 A, and they show no structure whatsoever.

Measurements of all the observed bands are recorded in Table IV. The limits of a band without a definite head are inclosed in

TABLE IV

Sulphur Dioxide

λ	λ Lowater	λ
.....	4163.0	2958
.....	4153.4	2945
.....	4145.5	.....
.....	4107.3	2938
.....	4040.6	2916.0
4010	4007.6	.....
3958	3954.6	2905
3861	3862.7	2893
3110	3811.3	.....
3760	3761.5	2885
3728	3726.5	2878.5
3677	3675.9	.....
3629	3628.0	2866
3546	3548.7	2861
3498	3502.3	.....
3429	3428.0	2829.1
3384	3383.7	2794.1
3273.3	3271.4	2781.9
3249.6	.....	2745.7
3166.5	.....	2700.5
3160.	.....	2665.5
3145	.....	2624.0
.....	.....	2590.3
3128	.....	2543.1
3125	.....	2517.1
.....	.....	2497.1
3104	.....	2472.8
3092	.....	2448.9
.....	.....	2436.1
3078	.....	2404.7
3065.6	.....	2388.5
.....	.....	2366.1
3059	.....	
3049	.....	2344.8
.....	.....	2323.8
3042	.....	2303.2
3028	.....	2284.3
		2265.8
3020	.....	2247.9
3008	.....	2224.2
.....	.....	.....
2998	.....	.....
2989	.....	.....
.....	.....	.....
2977	.....	.....
2969.1	.....	.....

brackets. These values are given in whole numbers for the very evident reason that the values are only approximations. The remaining numbers give the heads of bands which are degraded toward the red. Owing to the uncertainty of micrometer settings, caused by the continuous spectrum and by the small dispersion of the spectrograph in the visible and near ultra-violet, the longer wave-lengths recorded in the table are liable to be in error by as much as two or three angstroms. The absence of a sharp line termination of the heads of bands introduced some uncertainty in the settings made to the more refrangible side of λ 3000. A number of readings were taken for each head, however, and the average used. It is hoped that the average error in these results is not more than a few tenths of an angstrom, though this value may be exceeded in the extreme end of the spectrum, due to faintness of the bands.

Work has already been done by Miss Lowater[1] on the emission spectrum of sulphur dioxide. By the use of external electrodes, she passed a very feeble discharge through a tube containing sulphur dioxide, to which pure oxygen had been added to retard the decomposition of the compound gas. Spectrograms of the emission from this source, secured with a concave grating of 180 cm radius, showed eighteen bands degraded toward the red and lying between λ 4136 and λ 3271. Allowance being made for the greater accuracy of her measurements, a comparison of results serves to establish the identity of her bands with the ones in the more refrangible end of the present group. Accordingly, sulphur dioxide gives this group of bands under these different conditions, the present work having extended the limits of the group to double their former value.

This group of bands was slightly less intense with the gas flowing than at rest. This difference in intensity, however, may be due to change in the gas pressure, as the character of the discharge indicated such a change. No indication of the presence of the group on the exposure made with hydrogen sulphide was detected. Sulphur was also melted in a tube with a Bunsen flame and a discharge passed, but the photograph gave no evidence of the

[1] *Astrophysical Journal*, **23**, 338, 1906.

presence of this group in its spectrum. It accordingly seems very probable that this is the emission spectrum of sulphur dioxide.

SUMMARY

The visible band of ammonia is shown to be double with the more intense head on the side of shorter wave-lengths, as is also the case with the band in the ultra-violet. The present work, while not furnishing conclusive evidence, supports Lewis' suggestion that the ultra-violet band is due to some compound of nitrogen and hydrogen other than ammonia.

With oxides of nitrogen, the third positive group of nitrogen bands was observed from λ 3458 to λ 1902. The limits as given by Deslandres and by Schneiderjost for this group with air are from λ 3007 to λ 2154.

Deslandres' law apparently does not apply to the more refrangible end of the third positive group of nitrogen bands.

Bands of Deslandres' fourth positive group of carbon dioxide, which Hof failed to detect beyond λ 2215, were observed and measured, together with others beyond the limit given by Deslandres. These latter bands are the more refrangible ones of the group observed by Lyman in the Schumann region.

The study of the negative pole spectrum of carbon dioxide suggests that the first and second negative groups are due to different emission centers, the former probably being due to carbon monoxide and the latter to carbon dioxide.

Forty new bands were added to the emission spectrum of sulphur dioxide, thus increasing the number of bands from eighteen to fifty-eight and extending the more refrangible limit from λ 3171 to λ 2224.

In conclusion, I wish to thank Professor E. P. Lewis, under whose direction this work has been conducted.

UNIVERSITY OF CALIFORNIA
September 1920

ERRATA

Vol. **48,** December, 1918, "The Radial Velocities of 119 Stars Observed at the Cape," by Joseph Lunt:

Pages 270–75, Tables IV and V, delete the stars δ Ophiuchi, η Serpentis, and β Pegasi. The variations in velocity are fictitious and due to errors in the computation of the constants used in calculating the corrections to the sun.

[J. L.]

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